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TRANSLATION

INVESTIGATION OF INORGANIC SALTS FOR THE PURPOSE OF USING THEM
AS HIGH-TEMPERATURE LUBRICANTS

By

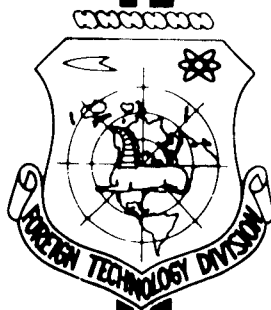
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THEM AS HIGH-TEMPERATURE LUBRICANTS

BY: M. M. Fialko and A. I. Dintses

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INVESTIGATION OF INORGANIC SALTS FOR THE PURPOSE OF
USING THEM AS HIGH-TEMPERATURE LUBRICANTS

by

M. M. Fialko and A. I. Dintses

In recent years there has been a sharp increase in the requirements with relation to thermal and thermo-acid stability of lubricating materials. One is confronted with the problem of maintaining high lubricating quality and at the same time creating lubricating materials which are capable of functioning at temperatures up to 600 or 800°C. In order to solve this problem much attention is being given to research in the field of solid lubricants and films obtained from graphite, molybdenum sulfide, metal oxides [1--3], etc. Processes have been developed for thermochemical treatment of friction surfaces, particularly sulfidation, where the ferrous alloys are treated with a mixture of salts in a bath with high temperatures [4, 5].

Judging by the data from the literature solid lubricants can work in the air at a temperature close to as high as 400°C. However, there is a requirement for new liquid lubricating materials which are stable at high temperatures. The principal advantage of a liquid lubricant lies in the fact that it assures removal of the heat from the friction surfaces and renewal of the lubricating material in the area of the friction.

Lubricating oils on the basis of petroleum decompose at temperatures below 200°C. Element-organic, above all silicon-organic liquids are much more stable. However, their use also is limited to temperatures up to 300 or 350°C.

This project is devoted to the seeking out among fusions of inorganic salts liquid lubricating materials which are capable of working up to 500°C. Inorganic salts possess high thermal stability, high boiling point, and good heat conductivity. It is not difficult to pick out salts or their eutectic

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mixtures stable at 500°C. In the integral of temperatures 200--500°C in the liquid state one finds mostly nitrates, nitrides, halides, and bichromates. One may point to the three-component mixture of nitrates and nitrites of sodium and potassium (nitrate-nitrite mixture) consisting of 53% KNO_3 , 40% NaO_2 , and 7% by weight of NaNO_3 [6--8], used as a heat conductor at industrial establishments [9]. The properties of inorganic salts as lubricating materials have been little studied. Some isolated reports are known in which information is to be found regarding moisture, corrosion action, and lubricating capacity of fused salts [10--17]. It is indicated that the corrosive action of fused salts depends on traces of ions of hydrogen which are present in the fusion. G. V. Vinogradov [16] notes that in the friction of steel on steel fusions of rhodanides behave like petroleum oil with sulfur additions. There are indications as to the possibility of the use of phosphates and phosphides as lubricating materials [18, 19].

Methods of Tests The determination of the corrosive action of fused salts was done in a quartz test tubes (Fig. 1) placed in a thermostat. Into

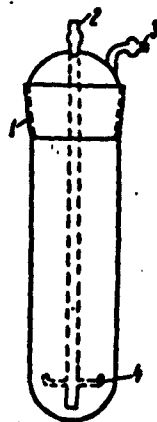


Fig. 1. Quartz test tube for determining corrosion
1--section; 2--air inlet; 3--air outlet, 4--extensions for suspension of plates

the tube the salt was put in which after its fusion the plates of the tested metal were inserted. Purified air was blown through the fusion. At the end of the test the salt was washed from the plates with water, and the water by alcohol. The corrosion was determined by the change

in the weight of the plates. For the corrosion tests there were chosen the alloyed steels EI347, R9K10, and 12KhN3A and the nickel alloys TsKB-1082R (type "niconel Kh") and NMZhMts-28-2,5-1,5 (type Monel metal).

For evaluating the hygroscopicity of the batch the salt was kept at 20°C

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in a dryer onto the bottom of which water was poured. The relative humidity in the dryer amounted to about 90%. The salt before the experiment was dehydrated at 20°C and a residual pressure of 5 mm on the Hg column. The crystal hydrates were preliminarily freed from the greater part of the crystallization water by heating at atmospheric pressure. Afterward the salts were carefully pulverized, weighed, and placed in the dryer in porcelain boats. The hygroscopicity was determined by overweight expressed in weight percentages.

The evaluation of the antiwear properties of the salts was done¹ on a four-ball apparatus with balls of the diameter of 12.7 mm made of silicon-molybdenum steel. The salts were ground in a porcelain mortar and dehydrated at 200°C and residual pressure of 5 mm on the Hg column, and up to the testing were kept in the dryer.

Results of the Tests The salt fusions differ sharply as to corrosive action. The least aggressive media of the investigated salts were the nitrates and the fluorides; the most corrosive were the chlorides and bromides, especially the chlorides and bromides of heavy metals (iodides of heavy metals, rhodanides, and other salts unstable at 500° were not tested). Fused salts at 500°C break down asbestos in the course of 5 hours (exceptions, K, Na, $\sim\text{NO}_3$) but protect graphite from oxydation by the oxygen of the water.

Hygroscopicity is an important characteristic of lubricating material. With lengthy preservation of an article with lubrication material corrosion of the article is possible. The presence of water in the salts leads to a sharp increase in the corrosion. The results of the obtaining of hygroscopicity of the salts are given in Table 2. The rate of absorption of moisture

¹In the laboratory of the All-Union Scientific Research Institute for the Processing of Petroleum and Gas and for the Production of Synthetic Liquid Fuel under the direction of V. A. Listov and V. A. Markov.

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by the salts decreases with time. The weakly hygroscopic salts (fluoride of lithium, bichromate of potassium) already in the first hours were completely saturated with moisture, after which the absorption stopped. Salts with high hygroscopicity were converted into watery solutions which absorb moisture from the air continuing to increase in volume. It is interesting to note that the hygroscopicity of of eutectic mixtures approaches that for the most

TABLE 1. Corrosive action of Fused Salts and Eutectic Mixtures (500°, 5 hr).

Salt or Eutectic Mixture	Change in the Weight of the Plates, mg/cm ²				
	ΔI347	R9K10	IMZhMts-28- 2.5-1-5	TsKB- 081R	12KhN3A
K, Na NO ₂ , NO ₃ *	+0.2	+0.4	+0.1	0	0
KNO ₃	+0.6	+0.4	+0.4	0	0
NaNO ₃	+0.5	+0.4	0	0	0
NaNO ₂	+0.1	+0.5	0	0	0
K, Na NO ₂	+0.5	+0.4	+0.4	0	0
LiNO ₃	+0.2	+0.4	+0.1	+0.1	-0.4
K ₂ Cr ₂ O ₇	0	0(-0.5)**	0	-0.3	(+0.2)
K, Li, Na F	+0.3	+0.2	0	-0.1	+0.2
Li, Na F, SO ₄	-0.3	0	0	+0.1	+0.1
	(+0.3)				-0.9(0)
K, Li, Na Cl	-0.9	-1.0(-0.1)	-0.3	-0.1	-2.6
	(-0.2)				(-1.7)
K, Na, Zn Cl	-8.5	-6.6(-6)	-0.3	0	-0.7
	(-10)				-1.0
K, Li Br	-4.0	-1.7	-0.5	0	-1.0
Cd, K, Na Br	-8	-1.7(-0.4)	-0.2	-0.1	(-0.4)
	(-0.6)				

*Here and from here on by the designation of salt system one understands the lowest-fusible mixture of a given system.

**In the cases where the results obtained in the blowing of air through the salt are considerably different from the results obtained without blowing the air through, two figures are shown in the table; the first relates to the experiments with blowing the air and in the remaining cases there is given the average value of the corrosion.

hygroscopic component. The corresponding data are given in Table 3.

The antifriction properties of salts (Figs. 2--5) are evaluated mainly at room temperature. The high temperatures and fusion of the salt influence the antiwear properties, however, the curves referring to different temperatures

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TABLE 2. Hygroscopicity of Some Salts and Their Eutectic Mixtures

Salt or Eutectic Mixture	Increase in weight, % for				
	0.5 hr	1 hr	2 hr	3 hr	44hr
KNO ₃	0.10	0.23	0.24	0.30	0.30
NaNO ₃	0.60	1.1	1.4	2.3	3.1
NaNO ₂	1.5	2.8	5.5	8.1	11
K, Na NO ₃ , NO ₂	1.5	2.9	5.4	8.2	9.9
K ₂ Cr ₂ O ₇	0.01	0.04	0.04	0.04	0.04
LiF	0.07	0.10	0.10	0.10	0.10
NaF	0.32	0.42	0.50	0.50	0.50
KF	2.0	5.6	11	15	20
K, Li, Na F	2.4	4.7	8.5	12	16
Li, Na F, SO ₄	0.80	1.4	2.5	3.4	4.8
NaCl	0.63	1.1	2.3	3.5	4.5
KCl	0.75	1.5	2.8	4.2	5.1
CdCl ₂	8.9	17	31	44	55
LiBr	4.9	9.0	15	22	28
NaBr	4.7	5.1	9.0	13	16
KBr	0.89	1.8	2.5	3.2	3.7
CdBr ₂	0.8	1.1	2.0	3.1	4.0
K, Li Br	3.0	5.9	12	16	21
Cd, K, Na Br	0.90	1.4	2.5	3.4	4.8

pass close to each other (Fig. 2). The divergence in the results obtained in the investigation of chloride and bromide of lead and also the eutectic of K-, Na-, and ZnCl at 20 and 250°C does not go beyond the error of experiment. Therefore in the graph there is plotted one curve for each of these salts. Of the number of salts studied the best antiwear properties are possessed by the chlorides, bromides and tungstate of potassium. For comparison in Fig. 3 there are shown the antiwear properties of the oil MK-8 evaluated under the same conditions. All the chlorides investigated and the bromides surpass in antiwear properties this petroleum oil.

The data presented show that there exist no salts which possess all the necessary properties for lubricating material. The salts with good antiwear characteristics have high corrosive action, and on the other hand the weakly corrosive salts possess poor antiwear properties. The improvement in the separate characteristics of the salts by mixing them with other salts is made difficult by the weak mutual solubility of the salts and because of the undesirable interaction between the salts. Nevertheless for determined conditions of work it is possible to select lubricating materials on

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TABLE 3. Hygroscopicity of Eutectic Salts and Their Components

Salt or eutectic mixture	Increase in 4 hr, %	Salt or eutectic mixture	Increase in 4 hr, %	Salt or eutectic mixture	Increase in 4 hr, %	Salt or eutectic mixture	Increase in 4 hr, %	Salt or eutectic mixture	Increase in 4 hr, %
$\text{Ca}(\text{NO}_3)_2$	24	KCl	5	KCl	5	LiNO_3	24	K_2SO_4	0.04
KNO_3	0.3	LiCl	35	NaCl	4.5	NaNO_3	3.1	ZnSO_4	10
LiNO_3	21	NaCl	4.5	ZnCl_2	29	Li, Na, Zn NO_3	23	K, Zn SO_4	9.5
Ca, K, Li NO_3	21	K, Li, Na Cl	33	K, Na, Zn Cl	25				

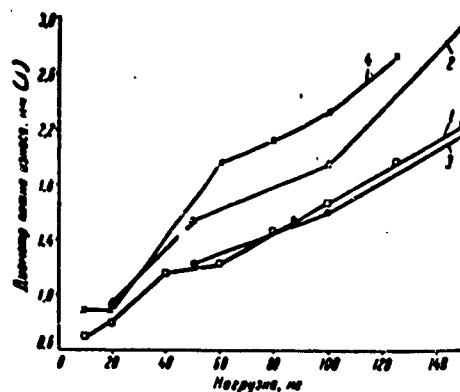


Fig. 2. Antiwear properties of nitrates

1--K-, NaNO_3 , NO_2 at 20° C (powder);
 2--K-, NaNO_3 , NO_2 at 250° C (fusion);
 3--K-, NaNO_3 , NO_2 at 500° C (fusion);
 4-- LiNO_3 at 20° C (powder).

Legend: (1) diameter of wear spot, mm

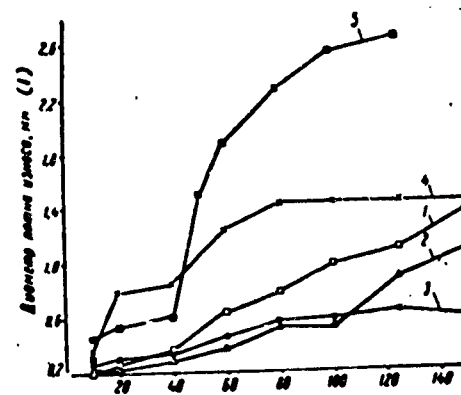


Fig. 3. Antiwear properties of chlorides at 20°C

1--NaCl; 2--KCl; 3--K-, Na-, ZnCl ;
 4-- PbCl_2 ; 5--MK-8.

Legend: (1) diameter of the wear spot, mm

a salt base. For example, in making use of lubricating materials, among them fusions of salts, in antifriction bearings their antiwear properties determined on a four-ball apparatus, do not have decisive significance. At the same time there may be great significance in this case in their high thermal stability.

Conclusions A study has been made of the corrosive action, hygroscopic property and antiwear property of a number of inorganics salts and their mix-

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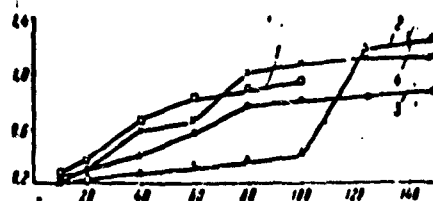


Fig. 4. Antiwear properties of bromides at 20° C.

1--K-, LiBr; 2--CdBr₂; 3--Cd, K-, NaBr; 4--PbBr₂.

Legend: (1) diameter of wear spot, mm

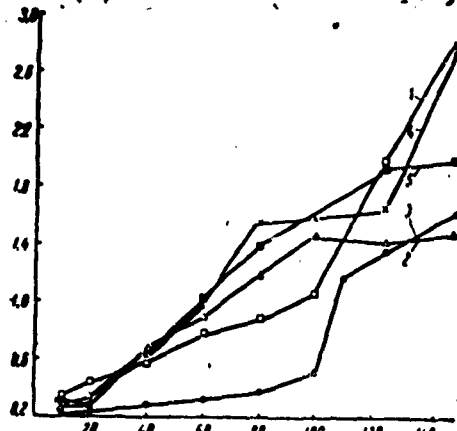


Fig. 5. Antiwear properties of fluorides, sulfates, and tungstates at 20° C

1--LiF; 2--K-, Li-, NaF; 3--K₂WO₄; 4--K₂SO₄; 5--Li-, NaF, -SO₄

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tures. The nitrates are much less corrosive than the chlorides and bromides. By their hygroscopic quality their eutectic mixtures come near to being the best hygroscopic component. The best antiwear properties among the salts studied are had by the chlorides and bromides, which exceed in this respect the mineral oil MK-8.

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